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# ANNUAL REPORT OF THE DIRECTOR OF THE FIXED NITROGEN RESEARCH LABORATORY

UNITED STATES DEPARTMENT OF AGRICULTURE,
FIXED NITROGEN RESEARCH LABORATORY,
*Washington, D. C., September 13, 1926.*

SIR: I have the honor to submit the annual report of the Fixed Nitrogen Research Laboratory for the fiscal year ended June 30, 1926.

Respectfully,

S. C. LIND,
*Associate Director,*
*Acting for F. G. Cottrell, Director.*

Hon. W. M. JARDINE,
*Secretary of Agriculture.*

This is the seventh year of operation of the laboratory and its fifth year under the Department of Agriculture. The downward trend in the price of synthetic ammonia which set in last year has continued. The decisive step has not yet been taken in its introduction into fertilizer material, but with the plant capacity now finished and under construction, saturation for all uses outside of agriculture will have been reached. Operating experience and cost data will also have been accumulated sufficient to enable the producer to determine whether it is feasible to expand into the fertilizer field. Owing to the competition that will be met in by-product ammonia, the progress of expansion may be delayed, but unless by-product ammonia production increases more rapidly than the use of nitrogen fertilizers, the entrance of synthetic ammonia into fertilizer material can not be long postponed. In any case the agricultural industry should be benefited by the competition.

The service which the laboratory renders to industry has continued to increase and one phase has expanded to the point of constituting a menace to the laboratory. Reference is made to the heavy draft which the synthetic ammonia industry has made upon the laboratory for technical men. Separations during the past year have amounted to between one-third and one-half of the entire technical staff; the average rate of increase in compensation was 55 per cent, the range being from 22 to 95 per cent increase. Although the training of technical men is regarded as one of the normal contributions of the laboratory in furthering the industry it may be questioned whether the laboratory can continue to support a draft at this rate. On the other hand, a very active and progressive state in the industry is indicated, both through the number of men needed and the salaries which the industry can afford to offer.

## THE DIRECT SYNTHETIC AMMONIA PROCESS

The direct synthetic ammonia process has expanded in the United States during the present year. Two new plants have been put into operation, two others are building, and one or two have increased their capacities. The plant which was put into operation last year, utilizing the laboratory's process and design, has operated successfully throughout the year. The long life of the catalyst has been especially gratifying. Although cost data have not been available, indirect estimates would indicate a very favorable cost.



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The introduction of the Claude process in this country by Lazote, the nitrogen subsidiary of the Du Pont Co., may be regarded as the most important development of the year. This process, although a modification of the original Haber process, nevertheless involves decided departures and many novel features. The operation pressure is 900 atmospheres. Water gas made directly from coal is the source of hydrogen, which is separated from carbon monoxide by means of the Claude refrigeration system. The successful operation of several units in the plant since early in 1926 marks one of the milestones of progress in the synthetic ammonia industry in the United States.

With the rapid development of the synthetic ammonia industry in this country the laboratory has been able to devote more of its time and energy to the consideration of the fundamental problems connected with it. The experimental work on the physical properties of compressed gas mixtures has been prosecuted vigorously. The compressibility of mixtures of hydrogen and nitrogen has been determined, as well as the saturation concentration of water vapor in the compressed gases. This type of investigation promises to become of increasing importance not only in supplying industry with important quantitative data but also as a theoretical contribution to our knowledge of the gaseous state at high pressures.

## PRODUCTION OF HYDROGEN

Owing to the importance of the item of cost of hydrogen for nitrogen fixation, the laboratory has continued to devote attention to the possibility of further improvements. Work has been continued on the production and testing of catalysts suitable for the water-gas reaction used to convert the carbon monoxide of water gas into hydrogen by the interaction of steam in the presence of a catalyst. Since this reaction produces carbon dioxide its removal by scrubbing with ammoniacal solutions of ammonium salts has been the object of a study, the results of which will be contained in a forthcoming publication. In connection with the purification of hydrogen an investigation has been made of the catalytic efficiency of certain materials for the removal of carbon monoxide by conversion to methane.

In industry the outstanding developments in hydrogen production have been (1) the decision of the Du Pont Co. not to recover hydrogen from coke-oven gases as a by-product but to use West Virginia coal for the direct production of water gas, which is then liberated and separated by the Claude system, and (2) the extension of the use of by-product hydrogen into a new field. In the bacterial action by which butanol is obtained, large volumes in equal proportions of carbon dioxide and hydrogen are evolved. Since the carbon dioxide can be readily separated, a pure form of hydrogen suitable for ammonia synthesis is at hand. The Commercial Solvents Corporation, of Peoria, Ill., is now having a 15-ton ammonia plant erected to utilize this source of hydrogen.

Another future possibility is the by-product hydrogen obtained in cracking gas for the production of carbon black. Some problems involved in this utilization have not as yet been worked out. The laboratory is carrying out some researches to that end.

## THE AMMONIA CATALYST

Progress has meen marked by the opportunity to observe the actual use of a laboratory catalyst under commercial conditions, on the one hand, and to extend the laboratory investigations into the fundamental aspects of contact catalysis. Results have been attained in both of these directions. The catalyst in commercial use appears to have a long life, the limit of which has not yet been determined, but will probably prove to be longer than a year under good operating conditions.

## METHODS OF NITROGEN CONVERSION

Of importance second only to the fixation of nitrogen is the conversion of the primary products of fixation into compounds which best meet the requirements of agriculture and the chemical industries. For fertilizer use, a salt of high nitrogen content which possesses suitable physical properties is most desirable. In this connection the laboratory has been carrying on development work on the synthesis of urea from ammonia and carbon dioxide. The work has been concerned with large-scale experiments with a small urea plant set up in conjunction with equipment for the production of hydrogen by the catalytic water-gas process. A novel feature of the urea process which involves the initial separation of carbon dioxide from the converted water gas and the subsequent separation of carbon dioxide and ammonia as part of the urea conversion cycle has been worked

out successfully by treating the gas mixtures with a solution of ammonium nitrate. Additional work remains to be done on the urea conversion itself which involves the reaction between carbon dioxide and ammonia at about 150° C. and under a pressure of about 100 atmospheres.

The oxidation of ammonia as the connecting link between ammonia and nitrates is growing in importance with the increased production of synthetic ammonia. In Europe much of the demand for nitrate nitrogen in agriculture and industry is now being supplied by this process, with the result that the consumption of Chilean nitrate has greatly decreased. This transformation process presents attractive possibilities for improvement, particularly as regards the conversion of the initial product of ammonia oxidation, nitric oxide, into nitric acid. The laboratory has continued its study of the reactions involved with a view of facilitating the recovery of the nitrogen oxides in usable form. Along the same line an investigation has been begun on the possibility of increasing the concentration of nitrogen oxides in the gases resulting from ammonia oxidation as a means of producing liquid nitrogen peroxide which could then be converted to nitric acid as a separate step. Preliminary studies have also indicated that liquid nitrogen peroxide may have attractive possibilities as a direct nitrating agent.

## GENERAL STUDY OF CATALYSIS

The fundamental study of catalysts and catalytic processes has been continued as a means of adding to our knowledge of catalytic reactions, which play such an important part in the nitrogen fixation problem. An investigation of the poisoning action of oxygen on ammonia catalysts has given us a much clearer picture of the nature of the catalyst surface and the effect of catalyst promoters. Information of importance in interpreting catalytic phenomena has also been furnished by a study of the decomposition of ammonia at low pressures.

## THE BACTERIAL FIXATION OF NITROGEN

Studies have been continued on the nature of the constitutents present in certain plant extracts and elsewhere, which act as growth promoters for legume-nodule bacteria. The data show that the active principle has many properties in common with water-soluble vitamin B, but its exact identity has not been established. It has been determined further that various strains of the legume bacteria respond differently to the active principle. With most newly isolated strains the response is slight, but after continued growth on artificial media containing the active principle the effect usually increases and in some instances the growth is many times greater than in its absence. An extensive study of the bacteria from the standpoint of nitrogen fixation when grown both in the presence and absence of the active principle has failed to show any definite proof that the organism uses free atmospheric nitrogen under any conditions except where growing in its normal environment in the root nodule. It seems, then, that both the legume plant and the bacteria play a vital rôle in the fixation process.

## EQUIPMENT

The high pressures of the direct synthetic ammonia process are new to American industry. Much of the equipment can not be obtained commercially and has to be specially designed. Some such equipment worked up by the laboratory has proved entirely satisfactory and is now available to and in actual use for other operations as well as for the production of synthetic ammonia.

### HIGH-PRESSURE CYLINDER CLOSURE

A type of closure, fashioned somewhat after the breech mechanism of the larger guns, has proven very successful for maintaining such gases as hydrogen and ammonia when subjected to the higher pressures and temperatures. This is a simple, positive type requiring but a flat metallic gasket. The pressure bolts, being in compression, in case of failure due to overstressing permit of easy release of the contained gas pressure rather than explosive release with its attendant hazards. This design is such that any expansion and contraction of the materials due to heating and cooling, which ordinarily cause a leak, are automatically and immediately compensated.

### RELIEF VALVE

Any system containing gases at high pressures should be safeguarded with efficient relief valves. No valves were available commercially for the pressure involved in ammonia synthesis. A valve has been developed which has proven valuable to other industries as

well. This valve can relieve thousands of times in succession, seating absolutely tight after each relief, thus protecting both life and equipment.

### ROD AND VALVE PACKING

Difficulty was experienced with commercial packings for pump and compressor operation at these pressures. It is very necessary, especially with a valuable and combustible gas like hydrogen, to prevent leakage. Such a packing is being worked up which is proving satisfactory. Unlike other packings, this one needs to be "made up" only hand tight and will still maintain hydrogen at the higher pressures without leak.

### PLATE VALVE

A plate valve developed for use in pumps operating at relatively high pressures has proven much more efficient than the ordinary poppet type of valve. This plate valve is of large diameter, thus necessitating an exceptionally small lift, permitting of a knife edge seat and thus line rather than surface contact.

## HIGH-PRESSURE COMPRESSOR

A small research-size compressor is being worked up for compressing gases to 15,000 pounds per square inch directly. This will permit of research work at such a pressure without the necessity of the slow method of compression through the medium of a water plunger. There is at this time no equipment of this nature commercially available.

Much other equipment for extreme conditions has been developed for both specific and general use. All these designs have been made available to the public, and wide use has been made of them by various industrial companies, both for commercial operation and research work. By having these designs available, organizations starting into research work on gases at higher pressures have saved considerable time.

## DIRECTOR'S VISIT TO EUROPE

The director of the laboratory made a trip to Europe in April, 1926, with the object of visiting nitrogen fixation plants in the various countries where this industry has been developed on a tremendous scale. The outstanding feature of the European situation appears to be the continued development of nitrogen fixation on an enormous scale. The synthetic-ammonia process continues to be the one most favored, and there has even been some conversion of cyanamide plant equipment to operate some of the newer methods of synthetic ammonia. Production of nitrogen compounds in Germany has already expanded beyond present needs and bids fair to do so in France and England. The consequent necessity for exportation has led to active sales propaganda, which was the keynote of the Biarritz conference. The Orient, principally India and China, seem to be regarded as the most promising outlet for the excess of European fixed nitrogen.

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